

2

OFFICE OF NAVAL RESEARCH

Contract N00014-89-J-1225

Technical Report No. 23

$^{15}\text{N}$  NMR POWDER SPECTRA OF SEMICRYSTALLINE NYLON 6

by

*Douglas G. Powell and Lon J. Mathias*

Submitted to

Polym. Commun.

Department of Polymer Science  
University of Southern Mississippi  
Southern Station Box 10076  
Hattiesburg, MS 39406-0076

DTIC  
ELECTE  
JUN 02 1989  
S E D

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

89 6 02 045

AD-A208 502

ADA208502

## REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION none			1b RESTRICTIVE MARKINGS none		
2a SECURITY CLASSIFICATION AUTHORITY none			3 DISTRIBUTION/AVAILABILITY OF REPORT  unlimited		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE none					
4 PERFORMING ORGANIZATION REPORT NUMBER(S)  Technical Report No. 23			5. MONITORING ORGANIZATION REPORT NUMBER(S)  ONR N00014-89-J-1225		
6a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Department of Polymer Science Hattiesburg, MS 39406-0076			7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 North Quincy Street Arlington, VA 22217-5000		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 North Quincy Street Arlington, VA 22217-5000			10 SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
11. TITLE (Include Security Classification) 15 N NMR Powder Spectra of Semicrystalline Nylon 6					
12. PERSONAL AUTHOR(S) Douglas G. Powell and Lon J. Mathias					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 6-1-88 TO 5-31-89		14. DATE OF REPORT (Year, Month, Day) 1989, May, 31	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION Submitted to Polym. Commun.					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT The solid state $^{15}\text{N}$ NMR chemical shift anisotropy (CSA) spectra of nylon 6 is reported. Nylon 6 (20% $^{15}\text{N}$ enriched) was prepared by anionic polymerization of isotopically enriched caprolactam. The samples observed were prepared by extraction with methanol to remove unreacted caprolactam, then either annealed to promote crystallization or artificially plasticized by immersion in molten caprolactam. The anisotropic linewidth was approximately 200 ppm, intermediate between the range reported for $sp^2$ and $sp^3$ hybridized nitrogens and consistent with the partial double-bond character of the carbon-nitrogen bond in amides. The individual components of the crystalline component tensor were calculated: $\sigma_{11} = 5$ ppm; $\sigma_{22} = 60$ ppm; $\sigma_{33} = 180$ ppm downfield of external glycine (0 ppm). The calculated isotropic chemical shift ( $\sigma_{\text{iso}}$ ) is 81.6 ppm, in good agreement with the value of 84.2 ppm obtained through MAS. At temperatures above $T_g$ , the amorphous region is seen as an isotropic peak which increases in intensity and narrows with increasing temperature. The effect of added plasticizer (caprolactam) contributes to this motional narrowing. At temperatures above 100°C, the most deshielded ( $\sigma_{\text{iso}}$ ) component is lost from the CSA spectrum suggesting a previously unreported motion occurring in the rigid crystalline region. This motion is postulated to be associated with the intermolecular hydrogen bond between adjacent chains.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION		
22a NAME OF RESPONSIBLE INDIVIDUAL Lon J. Mathias			22b TELEPHONE (Include Area Code) 601-266-4871		22c. OFFICE SYMBOL

## **$^{15}\text{N}$ NMR Powder Spectra of Semicrystalline Nylon 6**

Douglas G. Powell and Lon J. Mathias  
University of Southern Mississippi  
Hattiesburg, Mississippi 39406-0076

### **ABSTRACT**

The solid state  $^{15}\text{N}$  NMR chemical shift anisotropy (CSA) spectra of nylon 6 is reported. Nylon 6 (20%  $^{15}\text{N}$  enriched) was prepared by anionic polymerization of isotopically enriched caprolactam. The samples observed were prepared by extraction with methanol to remove unreacted caprolactam, then either annealed to promote crystallization or artificially plasticized by immersion in molten caprolactam. The anisotropic linewidth was approximately 200 ppm, intermediate between the range reported for  $sp^2$  and  $sp^3$  hybridized nitrogens and consistent with the partial double-bond character of the carbon-nitrogen bond in amides. The individual components of the crystalline component tensor were calculated:  $\sigma_{11} = 5$  ppm;  $\sigma_{22} = 60$  ppm;  $\sigma_{33} = 180$  ppm downfield of external glycine (0 ppm). The calculated isotropic chemical shift ( $\sigma_{iso}$ ) is 81.6 ppm, in good agreement with the value of 84.2 ppm obtained through MAS. At temperatures above  $T_g$ , the amorphous region is seen as an isotropic peak which increases in intensity and narrows with increasing temperature. The effect of added plasticizer (caprolactam) contributes to this motional narrowing. At temperatures above 100°C, the most deshielded ( $\sigma_{33}$ ) component is lost from the CSA spectrum suggesting a previously unreported motion occurring in the rigid crystalline region. This motion is postulated to be associated with the intermolecular hydrogen bond between adjacent chains.



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

# **$^{15}\text{N}$ NMR Powder Spectra of Semicrystalline Nylon 6**

## **INTRODUCTION**

The anisotropic chemical shifts (CSA) in solids can yield much information about the local electronic environment of a nucleus.<sup>1</sup> Although tensor elements have been estimated from the powder spectra of a number of  $^{15}\text{N}$  containing compounds,<sup>2,3</sup> only one single-crystal  $^{15}\text{N}$  study has been reported for an amide (glycylglycine) giving tensor orientations with respect to bond angles.<sup>4</sup> We are aware of no previous reports in the literature describing  $^{15}\text{N}$  chemical shift anisotropies of polyamides. This is not surprising since the random orientations of nuclei in semicrystalline polymers precludes absolute determination of tensor orientations with respect to the bond direction. Nevertheless,  $^{13}\text{C}$  CSA spectra of polymers have been shown to be sensitive to motions in the solid state.<sup>5</sup>  $^{15}\text{N}$  CSA spectra should be superior to  $^{13}\text{C}$  for probing nylon 6 since only one chemically distinct nitrogen is present in the polyamide repeat unit.

Recently, we have demonstrated that solid state CP/MAS NMR of natural abundance  $^{15}\text{N}$  is readily obtainable on solid polyamides.<sup>6,7</sup> The low sensitivity of natural abundance samples made relaxation experiments (e. g.  $T_1$ ,  $T_{1\rho}$ ) very time consuming. To circumvent this problem we prepared a  $^{15}\text{N}$  enriched sample of nylon 6, an important commercial polyamide which has been thoroughly characterized in the solid state by many techniques (DSC, IR, x-ray) including solid state  $^{13}\text{C}$  NMR.<sup>8,9</sup> The excellent sensitivity provided by this sample afforded us the opportunity to obtain the first static  $^{15}\text{N}$  chemical shift anisotropy spectra of a solid polyamide which we report here. Details of the polymer synthesis and  $^{15}\text{N}$  relaxation studies will be reported in a future paper.

## **EXPERIMENTAL SECTION**

**$^{15}\text{N}$  NMR.** Spectra were obtained on a Bruker MSL-200 NMR spectrometer operating at a field strength of 4.7 T and equipped with a Bruker MAS probe modified for obtaining static spectra with cross-polarization. The  $^{15}\text{N}$  resonance frequency was 20.287 MHz and that of the  $^1\text{H}$  was 200.13 MHz. Samples were placed in fused zirconia rotors fitted with Delrin caps. Crystalline glycine was used as an external chemical shift reference (0 ppm). Static spectra were obtained with a standard cross-polarization pulse sequence using a 3.5  $\mu\text{s}$   $^1\text{H}$  90° pulse and a mixing pulse of 2 ms. High power decoupling was used during a 50ms acquisition time with a nutating field of 62-68 KHz. Static spectra without cross-polarization were obtained using a 90°  $^{15}\text{N}$  pulse with decoupling during acquisition. The chemical shift anisotropy of static  $^{15}\text{N}$  spectra were simulated using POWDER, a Pascal program for simulating NMR lineshapes in solids and running on an Aspect 3000 computer.

## RESULTS AND DISCUSSION

A static  $^{15}\text{N}$  spectrum of nylon 6 prepared by anionic polymerization of caprolactam is shown in Figure 1, lower trace. The upper trace in Figure 1 shows the calculated CSA powder spectrum at 300K. The trace shows a non-axial shielding tensor approximately 200 ppm in width. This is in good agreement with the range reported for other amide nitrogens and reflects the partial double-bond character of the nitrogen in the amide group.<sup>4</sup> From POWDER calculations the individual tensors of the anisotropy were calculated:  $\sigma_{11}=5$  ppm;  $\sigma_{22}=60$  ppm;  $\sigma_{33}=180$  ppm. The calculated isotropic chemical shift ( $\sigma_{\text{iso}}$ ) is 81.6 ppm, in good agreement with the value of 84.2 ppm obtained through MAS.

The pattern shown in Figure 2, upper trace, is the same sample at 350K, i. e. slightly above  $T_g$ . A peak with relatively narrow linewidth is seen at approximately 87 ppm while the remainder of the spectrum is a typical pattern for a non-axial shielding tensor. The upper trace was obtained using the normal CP pulse sequence. The lower trace was obtained using a  $90^\circ$   $^{15}\text{N}$  pulse without CP. The crystalline components with long  $T_{1\rho}$  have become saturated in the lower spectrum with the resonance for the mobile fraction remaining.

It was thought that the narrow peak in the lower spectrum might be the result of plasticization of the amorphous component by caprolactam still dissolved in the sample (which should be a liquid at this temperature). To test this theory, two samples were prepared: one was extracted with methanol for 24 hours to remove residual  $^{15}\text{N}$ -caprolactam (unplasticized) while the other was extracted, then immersed in molten, unlabeled caprolactam at  $120^\circ\text{C}$  (replasticized).

Figure 3 shows the CSA spectra of the replasticized and unplasticized nylon 6 samples at two different temperatures. It can be seen that the isotropic resonance is more intense for the plasticized sample at any given temperature. The narrowing of the isotropic peak on addition of plasticizer gives clear evidence that plasticization is increasing the motional freedom of the amorphous fraction. The powder pattern for the crystalline fraction remains virtually unchanged at these temperatures.

$^{15}\text{N}$  CSA spectra of the extracted (unplasticized) sample were obtained for a series of temperatures as shown in Figure 4. At  $27^\circ\text{C}$ , the non-axial powder pattern is seen. As the temperature is increased, a narrow amorphous resonance appears centered near 84 ppm. This peak becomes narrower and more intense at higher temperatures and is clearly seen above  $100^\circ\text{C}$ . The chemical shift of the amorphous fraction (84.3 ppm) approaches the isotropic chemical shift obtained through MAS. Again, rapid motion has averaged the anisotropy of the amorphous fraction. However, higher temperatures are required to achieve the same motion that is observed in the plasticized nylon sample.

Another interesting phenomenon is observed in the CSA spectra of Figure 4. As the temperature is

increased from 27°C to 100°C, the downfield component of the powder pattern  $\sigma_{33}$  becomes smaller. At 115°C this component is either no longer sharply defined or has disappeared altogether. Note also that the  $\sigma_{22}$  and  $\sigma_{11}$  elements remain essentially unchanged from the room temperature spectrum. This indicates a retention of non-axial symmetry since, in an axially symmetric pattern, the  $\sigma_{22}$  and  $\sigma_{11}$  elements should average to some intermediate value.<sup>1</sup> Although the pattern remains non-axially symmetric, the loss of the  $\sigma_{33}$  component at elevated temperature suggests the onset of motion associated with this tensor component of the amide nitrogen.

Interestingly, the tensor element  $\sigma_{33}$  associated with this component has been shown to lie nearly parallel to the NH bond in amides.<sup>4</sup> This suggests a change or transition in intermolecular hydrogen bonding at elevated temperatures that apparently does not destroy the crystal structure. In the crystalline region of the polyamide, the relatively small hydrogen will have the best chance for rapid motion even in the solid lattice. The concept of a "mobile" hydrogen that oscillates at a frequency sufficient to attenuate the  $\sigma_{33}$  component alone is consistent with the remaining crystalline components of the CSA spectrum at 150 °C.

## CONCLUSIONS

The first chemical shift anisotropy patterns of a polyamide have been obtained on nylon 6. The CSA powder patterns show the growth of an amorphous signal at elevated temperatures with a chemical shift near the isotropic value obtained with MAS. The addition of plasticizer (caprolactam) causes this signal to grow in at lower temperatures confirming that plasticization is increasing molecular mobility in the amorphous region. The  $\sigma_{33}$  component becomes less prominent with increasing temperature and finally disappears above 115°C. The source of this component has not been previously reported, but is postulated to be motion associated with the tensor component along the NH bond of the amide group. We tentatively assign this motion to rigid vibrational libration of the hydrogen atoms in the still hydrogen-bonded crystalline portion of the sample.

## ACKNOWLEDGEMENTS

We gratefully acknowledge a Department of Defense instrumentation grant with which we purchased our Bruker MSL-200 spectrometer. This research was supported in part by a grant from the Office of Naval Research. Thanks also to Dr. William L. Jarrett for helpful discussions concerning the NMR pulse experiments used here.

## REFERENCES

1. Fyfe, C. A. "Solid State NMR for Chemists," C. F. C. Press: Guelph, Ontario, Canada, 1983, p. 201-02.
2. Valentine, K. G.; Rockwell, A. L.; Gierasch, M.; Opella, S. J. *J. Magn. Reson.*, **1987**, 73, 519.
3. Oas, T. G.; Hartzell C. J.; Dahlquist, F. W.; Drobny, G. P. *J. Am. Chem. Soc.*, **1987**, 109, 5962.
4. Harbison, G. S.; Jelinski, L. W.; Stark, R. E.; Torchia, D. A.; Herzfeld, J.; Griffin, R. G. *J. Magn. Reson.*, **1984**, 60, 79.
5. Jones, A. A. in "High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk," R. A. Komoroski, ed., VCH Publishers, Inc., Deerfield Beach, Florida, (1986), p. 261-74.
6. Powell, D. G.; Sikes, A. M.; Mathias, L. J. *Macromolecules*, **1988**, 21, 1533.
7. Mathias, L. J.; Powell, D. G.; Sikes, A. M. *Polym. Commun.*, **1988**, 29, 192.
8. Weeding, T. L.; Veeman, W. S.; Guar, H. A.; Huysmans, W. G. B. *Macromolecules*, **1988**, 21, 2028.
9. Kubo, K.; Takeshi, Y.; Tadashi, K.; Ando, I.; Shiibashi, T. *J. Polym. Sci.: Part B: Polymer Physics*, **1989**, 27, 929.

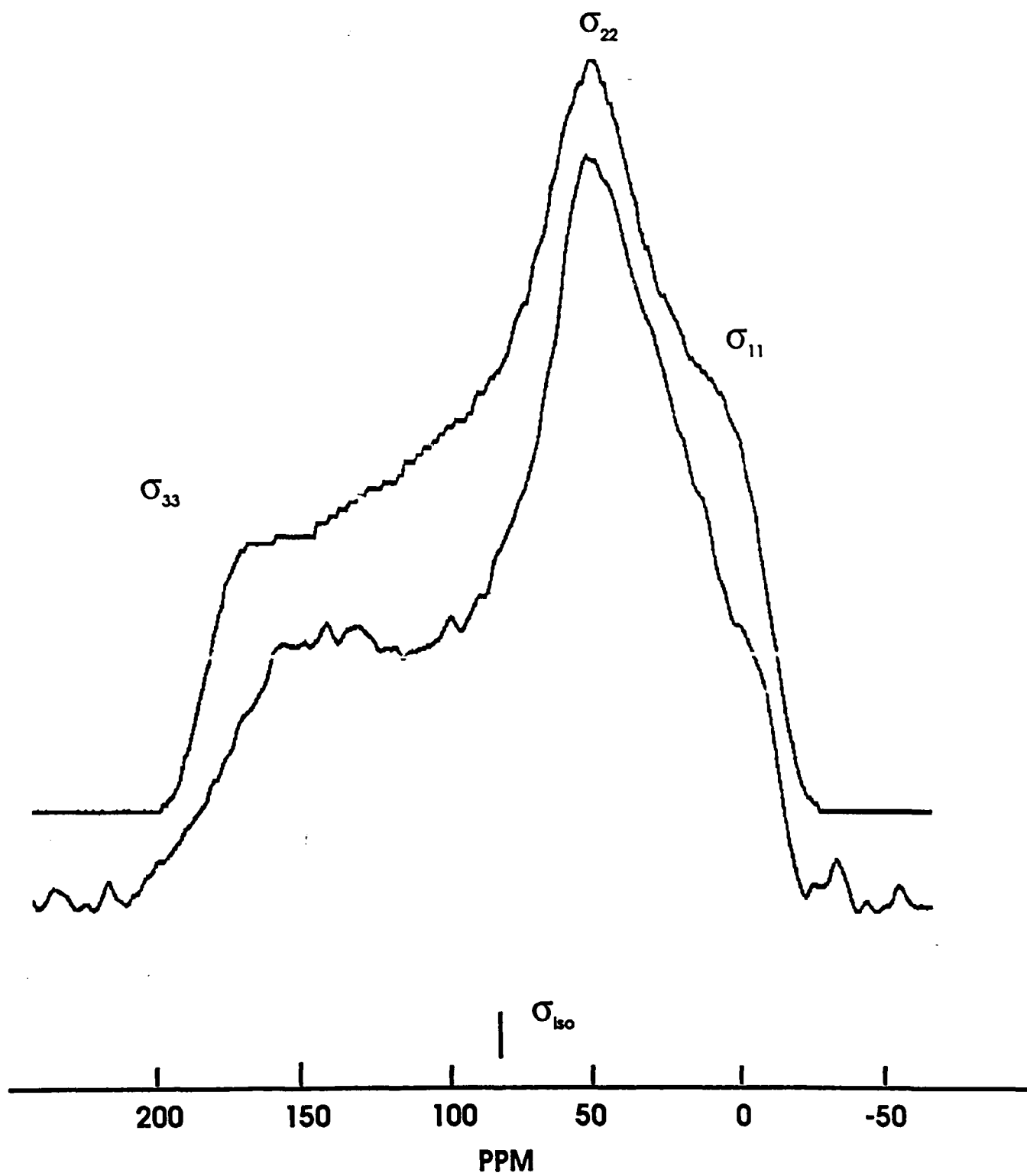
## LIST OF FIGURES

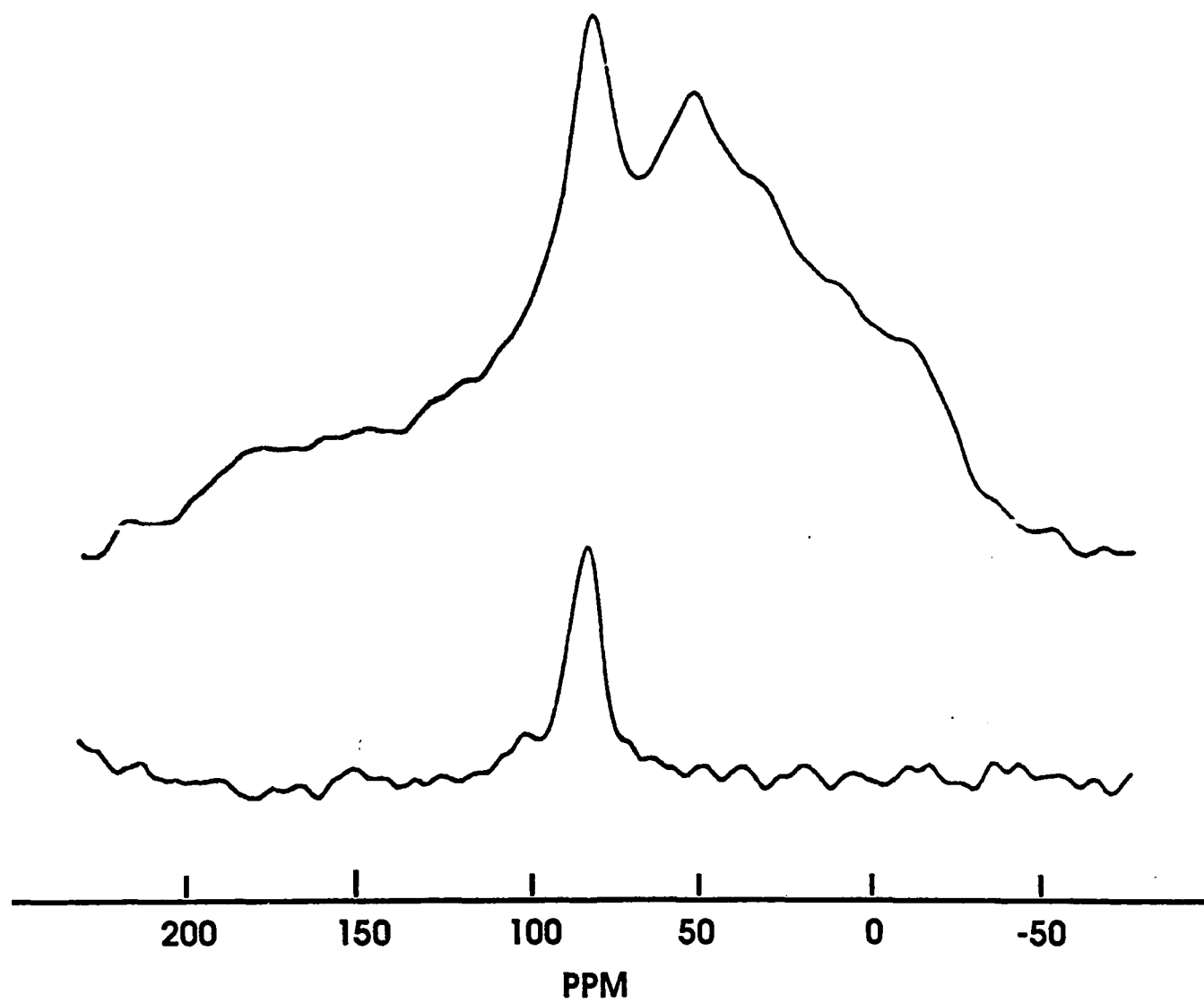
**Figure 1.** Static  $^{15}\text{N}$  CSA spectrum of methanol extracted sample at 300K. Upper trace is the best fit from POWDER showing the relative positions of the tensor components.

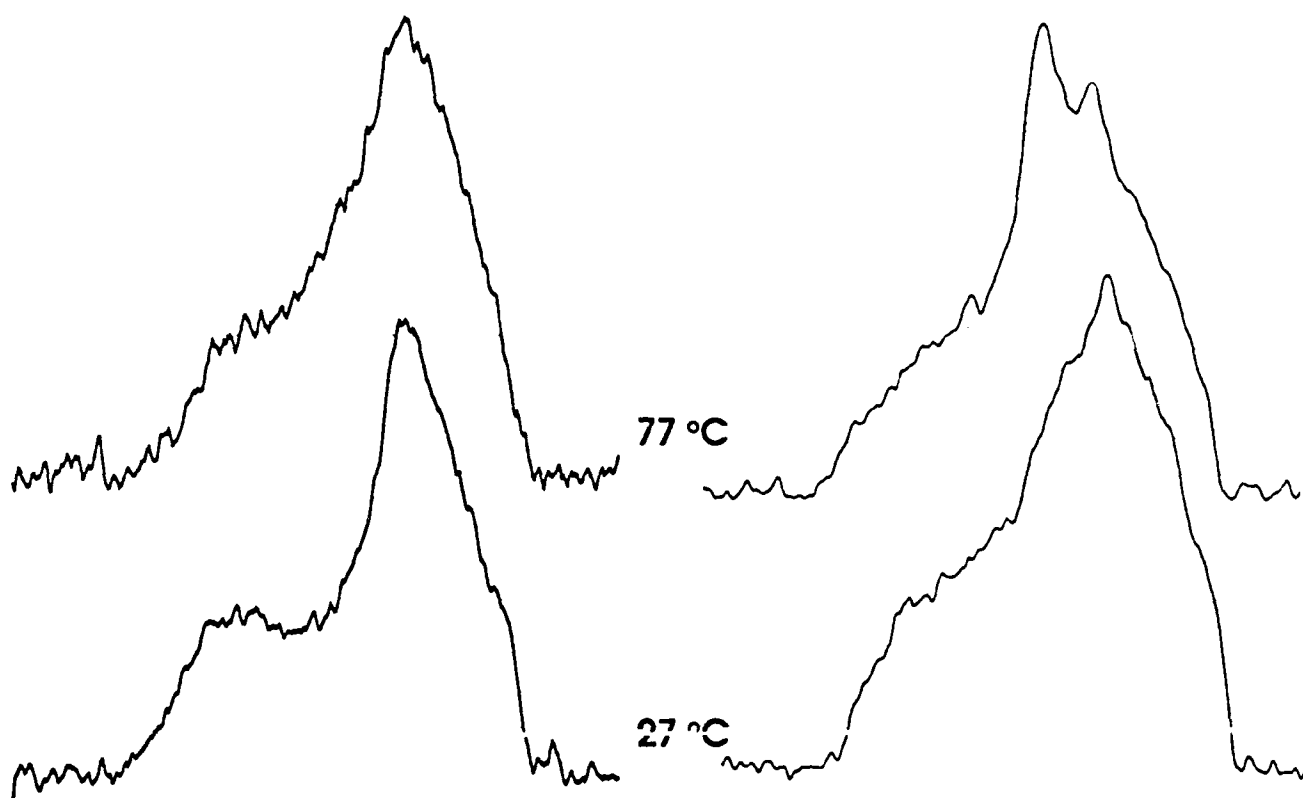
**Figure 2.** Static  $^{15}\text{N}$  NMR spectrum of in situ prepared nylon 6 at 350K. Top trace: CP spectrum showing both crystalline and non-crystalline components. Bottom trace: Spectrum obtained with a  $90^\circ$  pulse and decoupling showing non-crystalline components.

**Figure 3.**  $^{15}\text{N}$  CSA powder spectra of nylon 6. Left column: Methanol extracted samples (unplasticized by caprolactam); Right column: Samples plasticized by heating in molten caprolactam.

**Figure 4.** Static  $^{15}\text{N}$  NMR spectrum of annealed nylon 6 sample obtained with cross polarization and high power decoupling at different temperatures. The non-crystalline component at approximately 84 ppm becomes increasingly sharper at elevated temperatures.







**Unplasticized**

**Plasticized**

